A modelling view on the existence of hysteresis during reactive HiPIMS

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Dedicated Research on Advanced Films, and Targets

GHENT UNIVERSITY

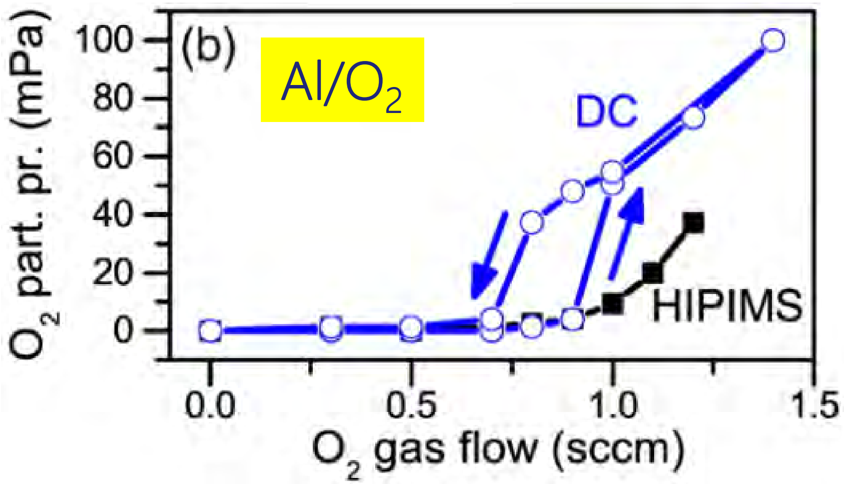
FACULTY OF SCIENCES

DRAFT

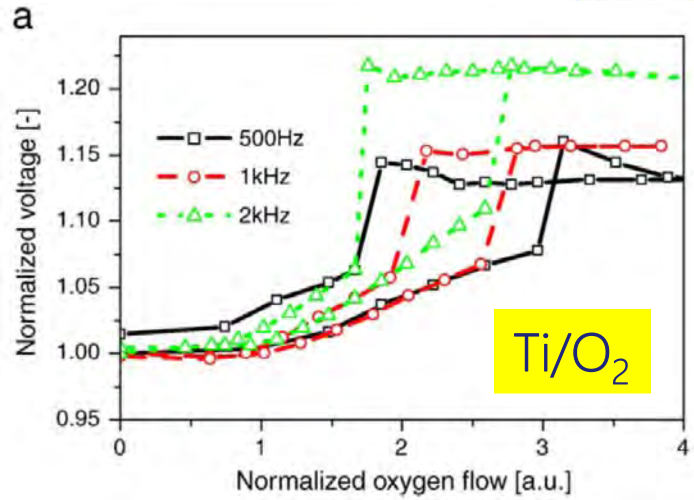
RSD 2016
Reactive sputter deposition

Outline

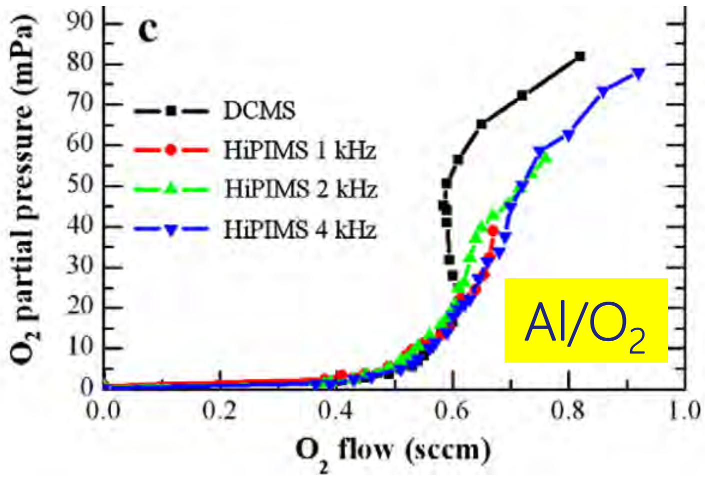
Reactive HiPIMS: hysteresis?



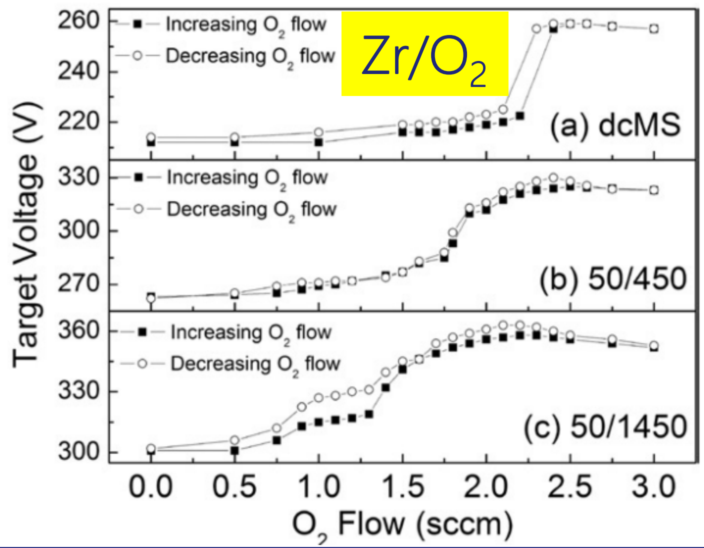
E. Wallin, et al., *Thin Solid Films 516*, 6398 (2008)



T. Kubart, et al., *Surf. Coat. Tech. 205*, S303 (2011)

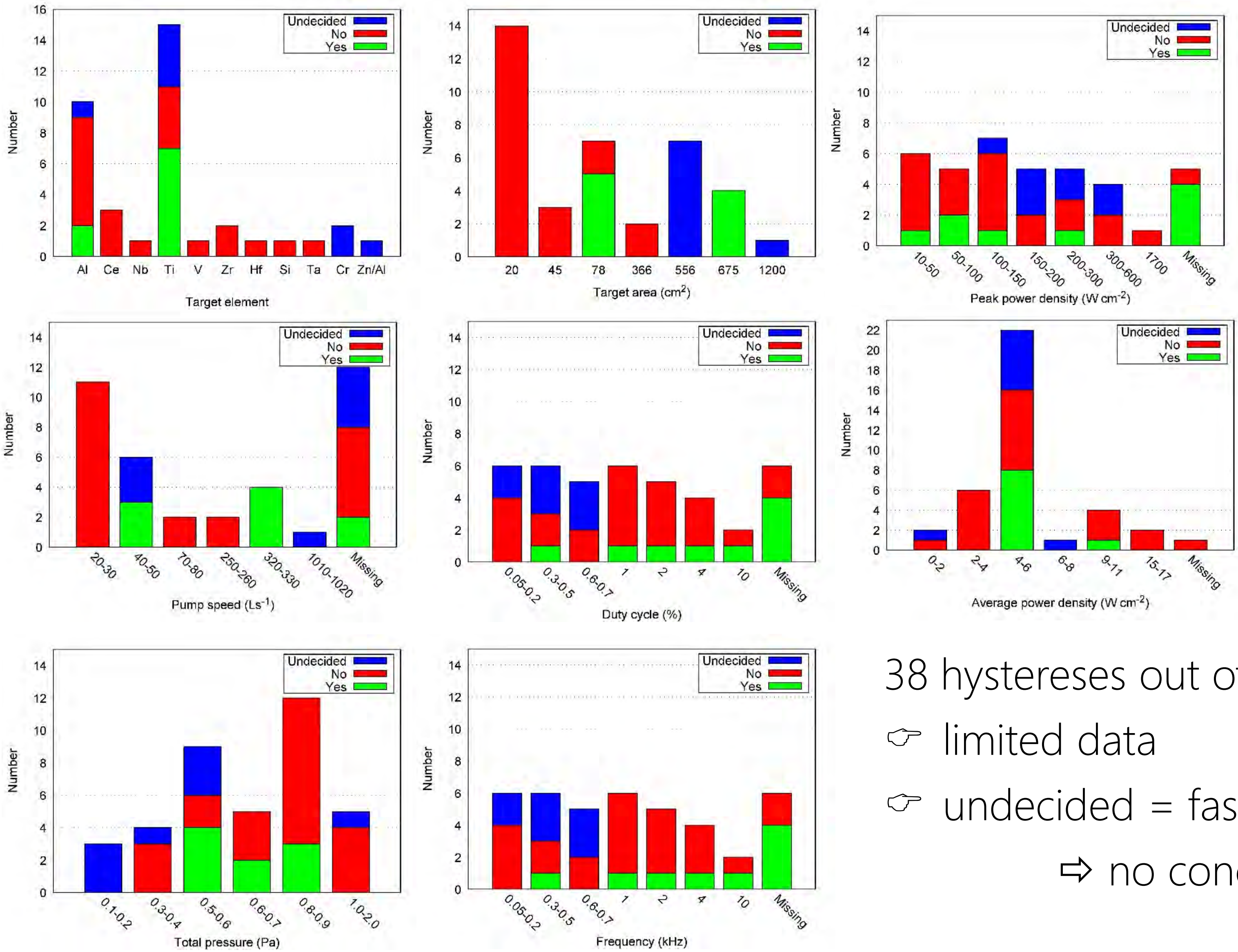


M. Aiempanakit, et al., *Thin Solid Films 519*, 7779 (2011)



K. Sarakinos, et al., *Surf. Coat. Tech. 202*, 5033 (2008)

Reactive HiPIMS: hysteresis?



Hysteresis?

9 yes

21 no

8 undecided

38 hystereses out of 18 papers

☞ limited data

☞ undecided = fast ramping

⇨ no conclusions

Outline

1. Introduction
2. RSD models
3. Simulation study
4. RSD+IR model
5. Conclusion

Variables in RSD model

System part	Resolved variable		Model approach
Chamber	P Q_p	reactive partial pressure gas flow to pump	one-cell
Target •Surface • Subsurface	Q_t θ_m θ_c θ_r $n_m(x)$ $n_r(x)$	gas flow consumption metallic fraction chemisorbed fraction reacted fraction metal concentration reactive gas concentration	one-cell uniform current multi-cell non-uniform current depth profile SRIM implantation
Substrate	θ_s Q_s	chemisorbed fraction gas flow consumption	one-cell multi-cell SIMTRA profile

5 BALANCE equations ⬄ 5 ODE's

$$0 = f(y) \leftrightarrow \frac{dy}{dt} = f(y)$$

Steady state ⬄ Time

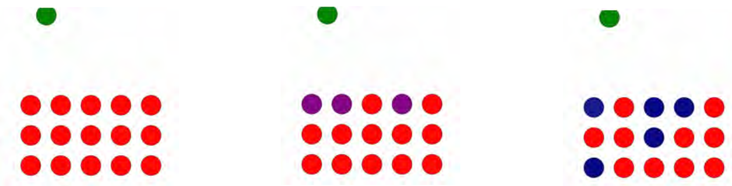
2 ODE's ⬄ 2 PDE's

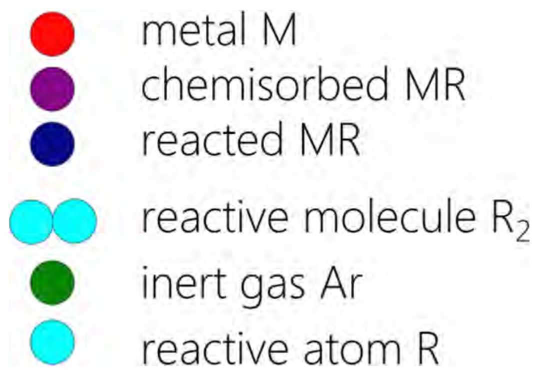
$$0 = f\left(y, \frac{\partial y}{\partial x}\right) \leftrightarrow \frac{\partial y}{\partial t} = f\left(y, \frac{\partial y}{\partial x}\right)$$

Processes in RSD2013

Target

sputtering

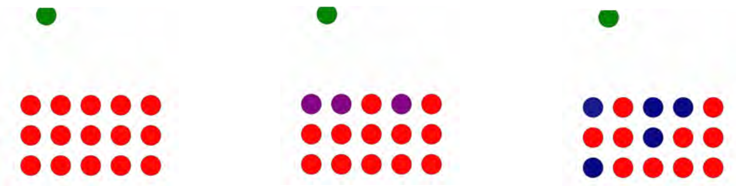


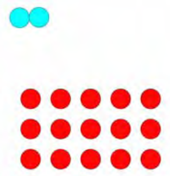


Processes in RSD2013

Target

sputtering





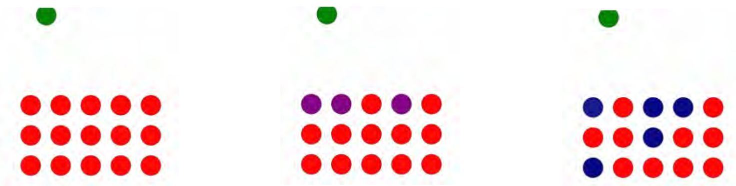
direct implantation

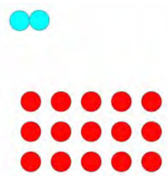
metal M
chemisorbed MR
reacted MR
reactive molecule R_2
inert gas Ar
reactive atom R

Processes in RSD2013

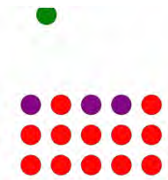
Target

sputtering





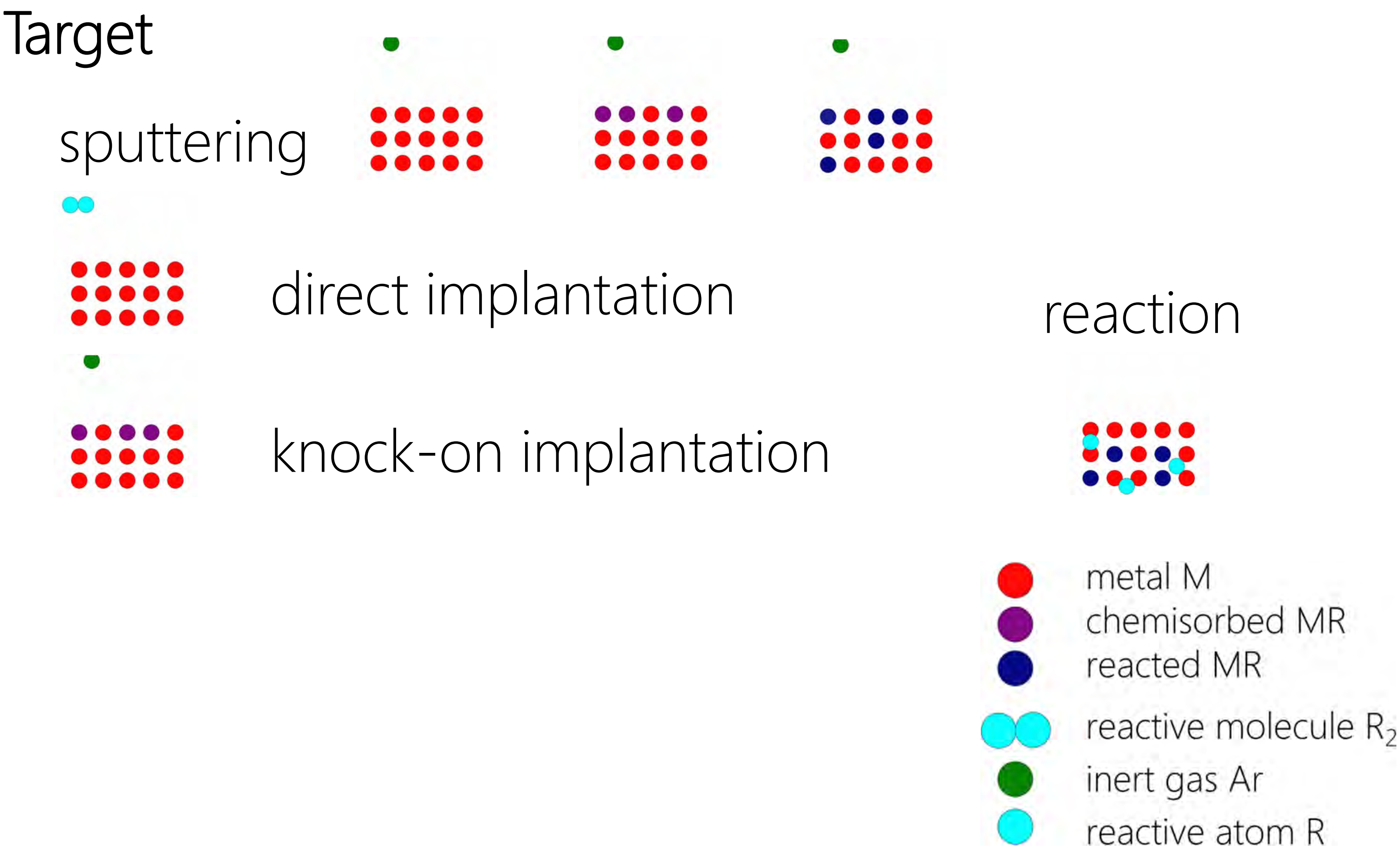
direct implantation



knock-on implantation

metal M
chemisorbed MR
reacted MR
reactive molecule R_2
inert gas Ar
reactive atom R

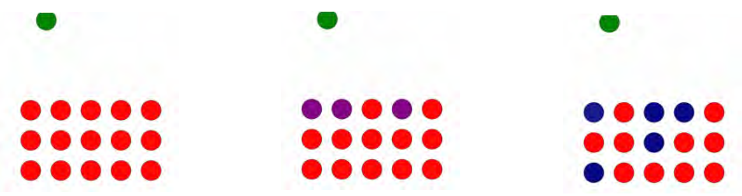
Processes in RSD2013

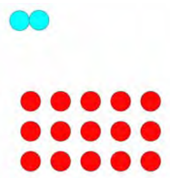


Processes in RSD2013

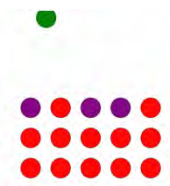
Target

sputtering



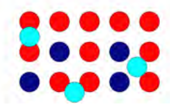


direct implantation



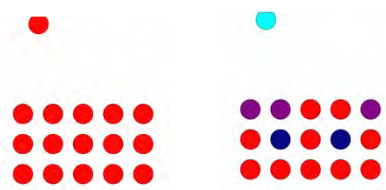
knock-on implantation

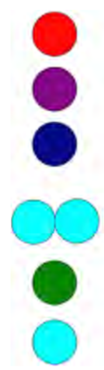
reaction



Target & substrate

deposition





metal M
chemisorbed MR
reacted MR
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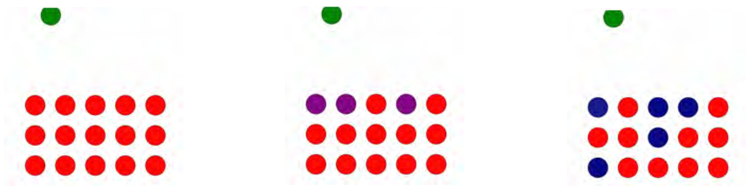
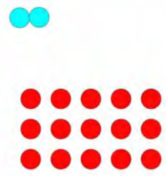
Processes in RSD2013

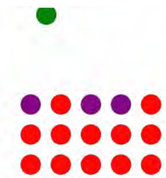
Target

sputtering



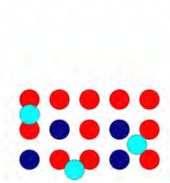


direct implantation



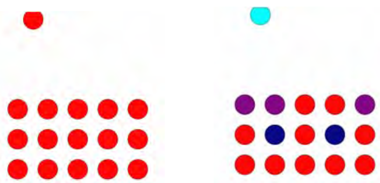
knock-on implantation

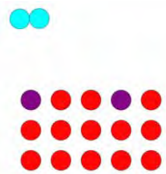
reaction



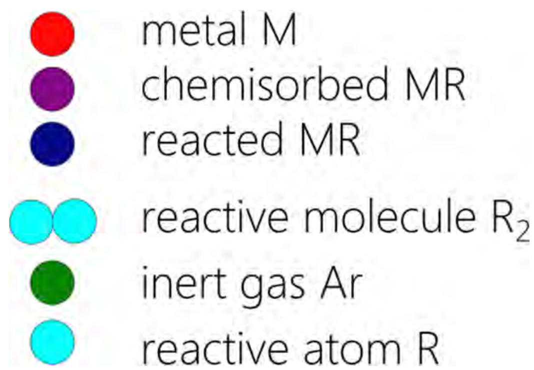
Target & substrate

deposition



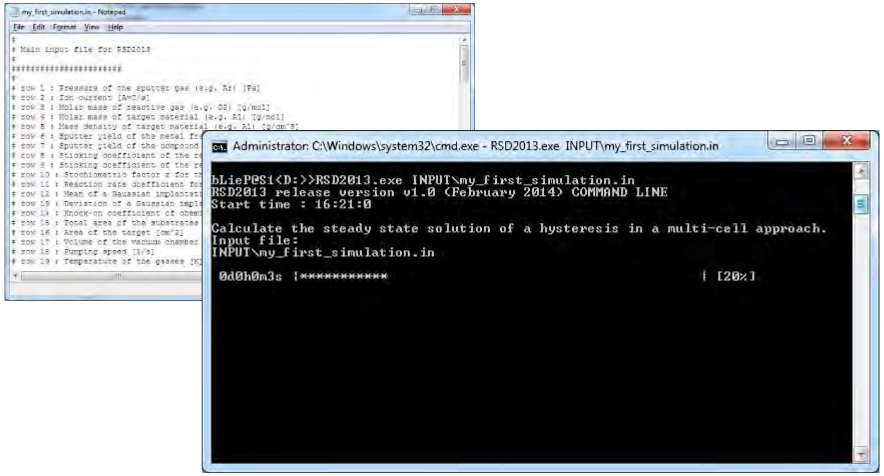


chemisorption

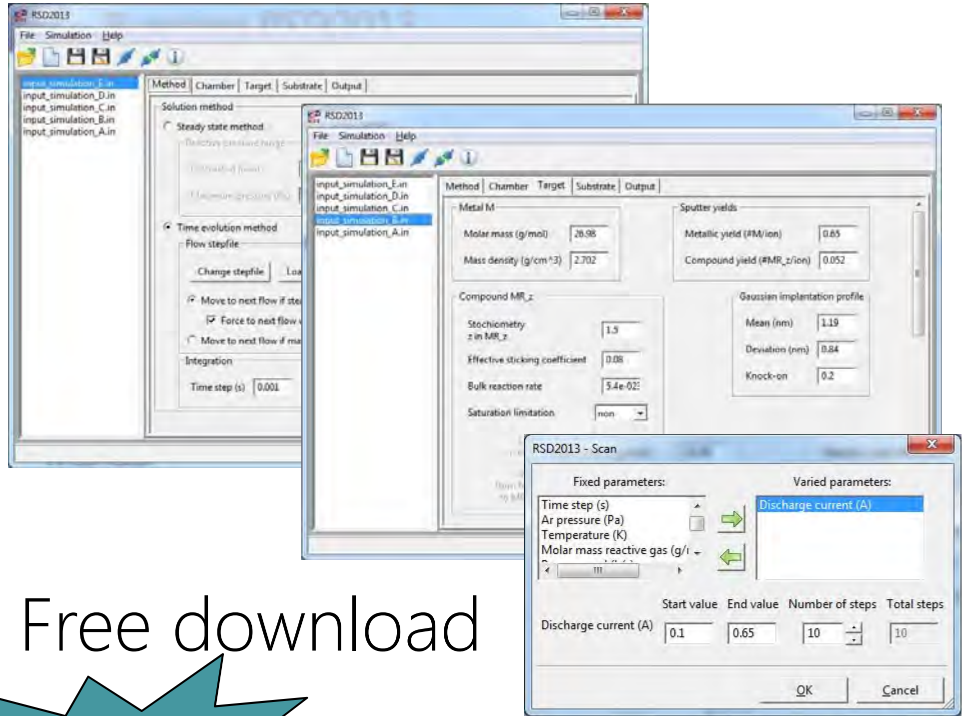


Running RSD2013 software

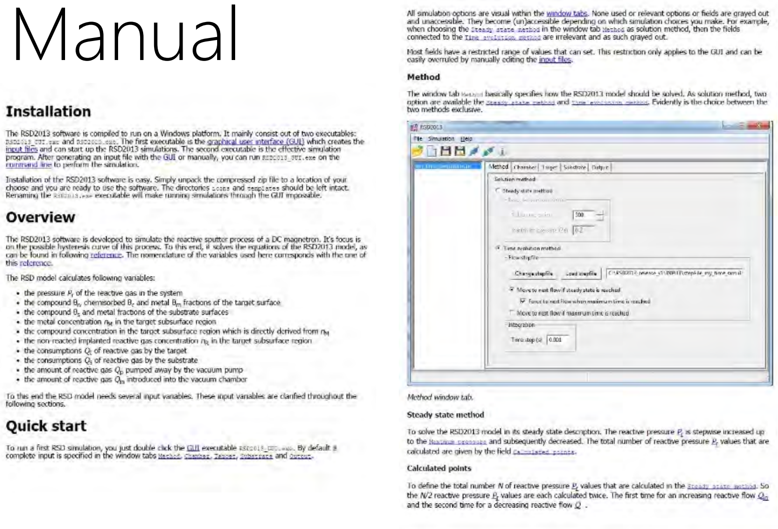
Command line



Graphical user interface (GUI)



Manual



Free download

SRIM
www.srim.org

SIMTRA v2.2.1-beta
www.DRAFT.ugent.be

RSD2013 v1
www.DRAFT.ugent.be

Extension of the RSD model to HiPIMS

Model modifications ...

- **RSD^{+P}**
  (squared blocked) current pulses
  ☞ inherent time dependent (only time solution)

- **RSD^{+PR}**
  Different oxygen 'activation'
  ☞ sticking coefficient lowers during pulse off-time

- **RSD^{+PM}**
  Metal ionization and implantation
  ☞ combined ionization-return probability ε_{M+} for sputtered metal atom
  ☞ metal implantation profile
  ☞ density relaxation is included

Study the effect on the hysteresis of ...

- Enhanced target cleaning?
- Lower surface reactivity by pulse off-time (and gas rarefaction)
- High dose of metal implantation

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Reference system

Start from a reference DC system of Al in Ar/O_2

Parameters	Value	Description
RSD		
Y_m [#M(R_z) ion^{-1}]	0.756	sputter yield of metal atoms M
Y_r, Y_c [#M(R_z) ion^{-1}]	0.06	sputter yield of compound molecules MR_z, chemisorbed molecules MR_z
α_t	0.1	sticking probability of reactive gas on metal for target
α_s	0.1	sticking probability of reactive gas on metal for substrate
k [cm^3 s^{-1} #M(R_z)$^{-1}$]	$5\cdot10^{-23}$	reaction rate coefficient of implanted reactive atoms with metal particles
β [#R ion^{-1}]	0.2	knock-on yield of chemisorbed reactive atoms
p(x) [cm^{-1}]	R_p=1.4 nm dR_p=0.8 nm	mean of Gaussian implantation profile of reactive atoms deviation of Gaussian implantation profile of reactive atoms
n_0 [#M(R_z) cm^{-3}]	$6.03\cdot10^{22}$	particle density
z	1.5	stoichiometric factor
I [A]	0.286	discharge current
P_i [Pa]	0.4	inert working gas pressure
T [K]	300	gas temperature
V [cm^3]	12500	volume of vacuum chamber
A_t [cm^2]	10	area of target
A_s [cm^2]	1000	area of substrate
S [L s^{-1}]	48.54	gas pumping speed

Low sticking probability

Constant current mode

Average power

- metallic mode ~100 W
- poisoned mode ~70 W

Relative low working pressure

Keep it simple:

- one-cell target
- one-cell substrate

Operation pressure Argon

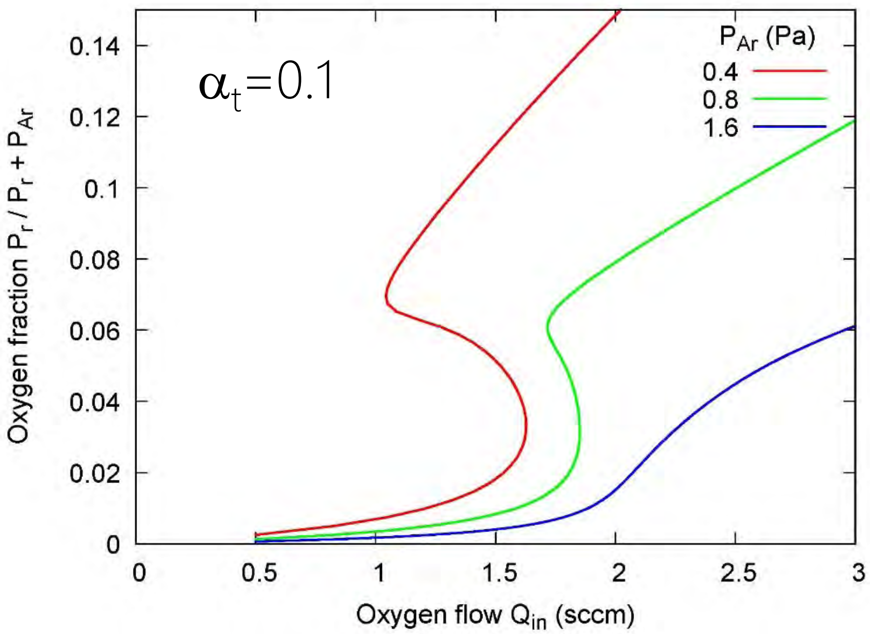
RSD

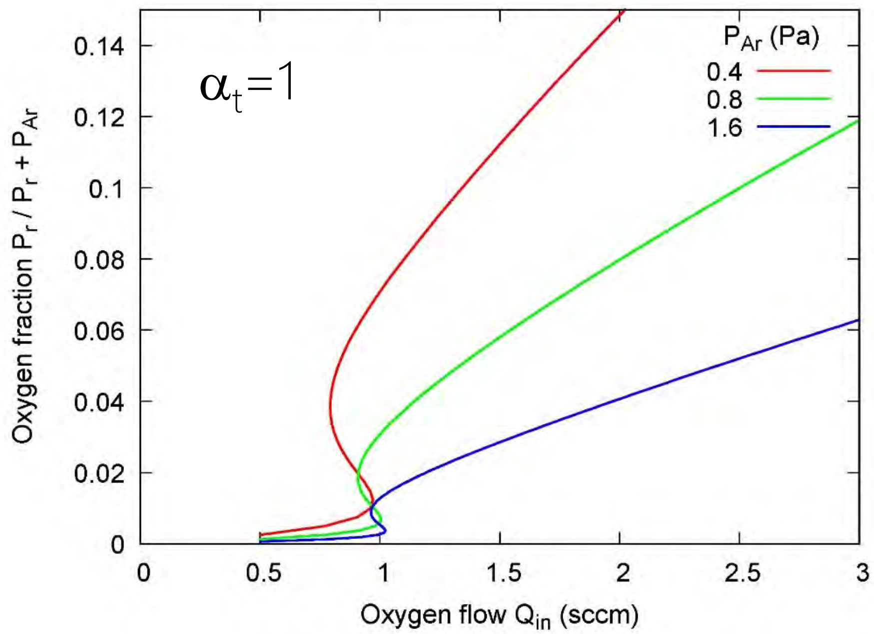
What's the influence of the working pressure in DC ?

☞ depends on surface reactivity of gas on target material

☞ hysteresis vanishes for low surface reactivity (like Al and Ti) at higher working pressure

⇨ HiPIMS "often" at higher working pressure





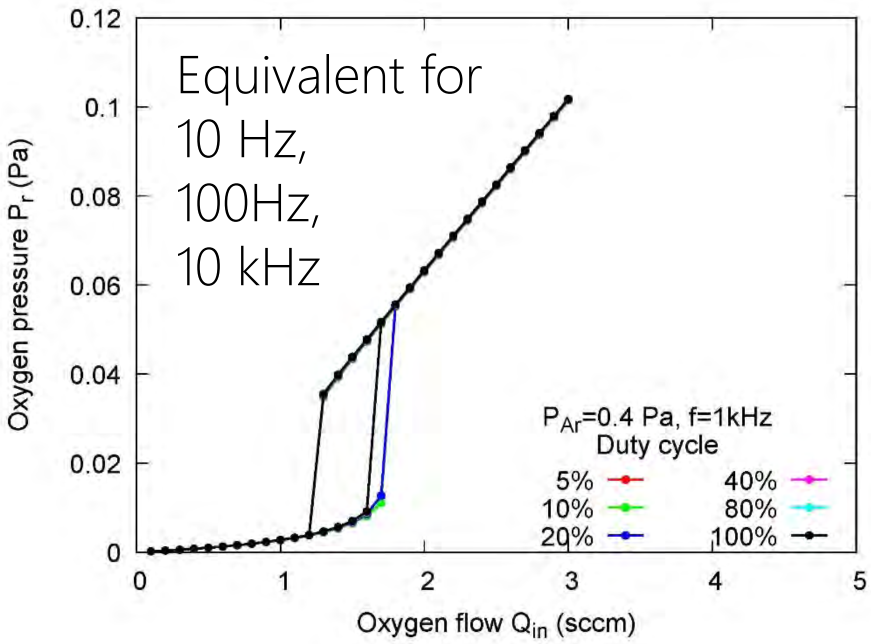
Current pulses

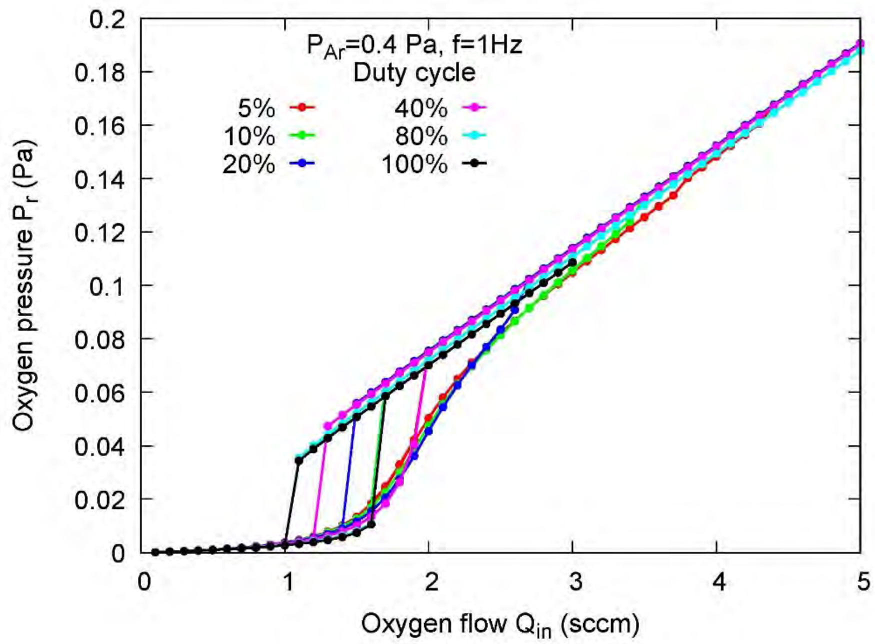
RSD^{+P}

What's the influence of the current pulses?

- characterized by frequency *f*, duty cycle *d* and pulse *p* (=d/f)
- typical HiPIMS frequencies (100 Hz-10 kHz) and duty cycle (1-10 %)
- only effect at order 1 Hz

⇨ reactive time dynamics are slower (~1s)

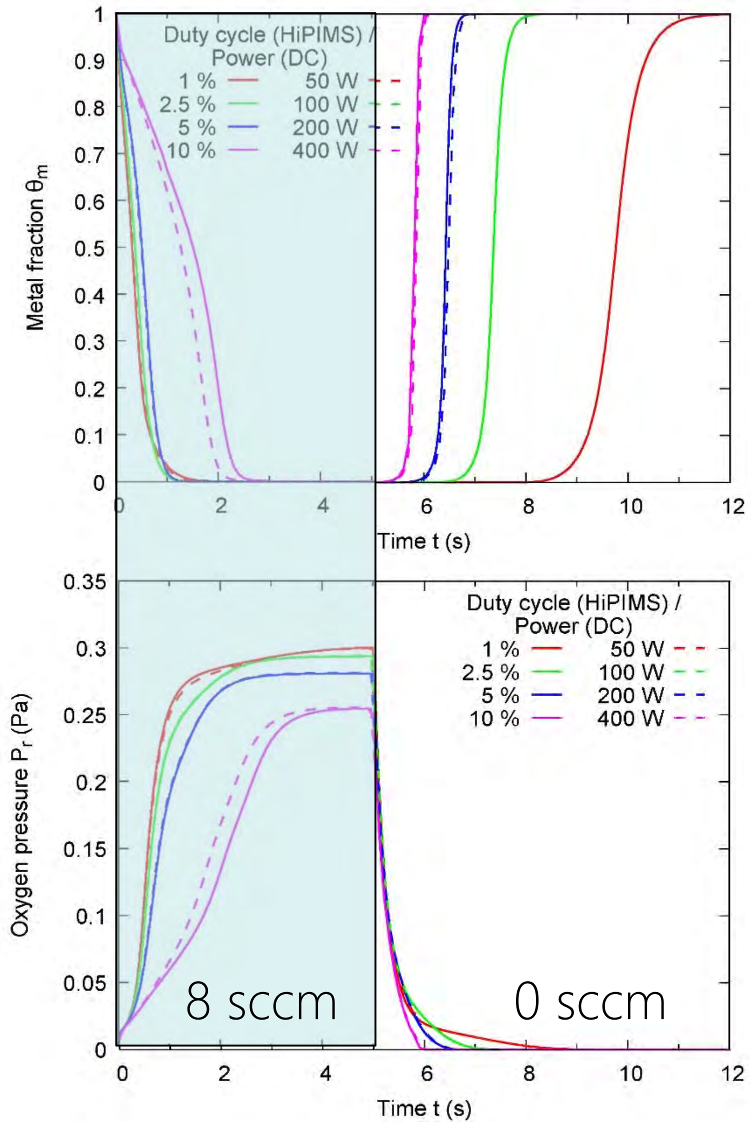




constant average power 100 W

Target cleaning

RSD^{+P}



Time dynamics of target poisoning and sputter cleaning for DC and for HiPIMS (f=1kHz)

What's the influence of the average power?

☞ Similar as for the DC regime
- cleaning time scales inversely with power
- poisoning time is only at higher power prolonged

☞ Way of power delivery only starts to matter at high power

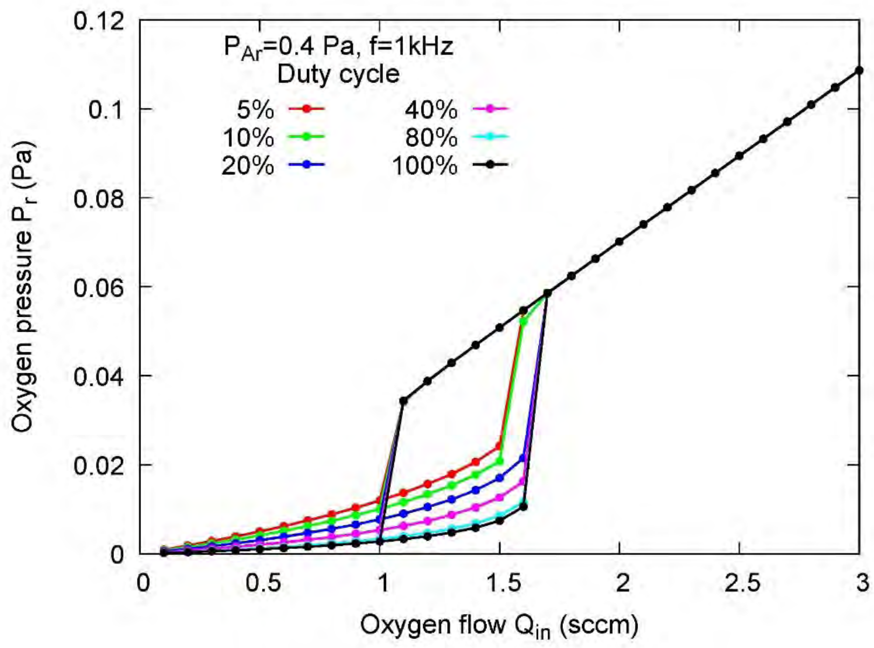
☞ Depoisoning target retarded compared to reactive pressure

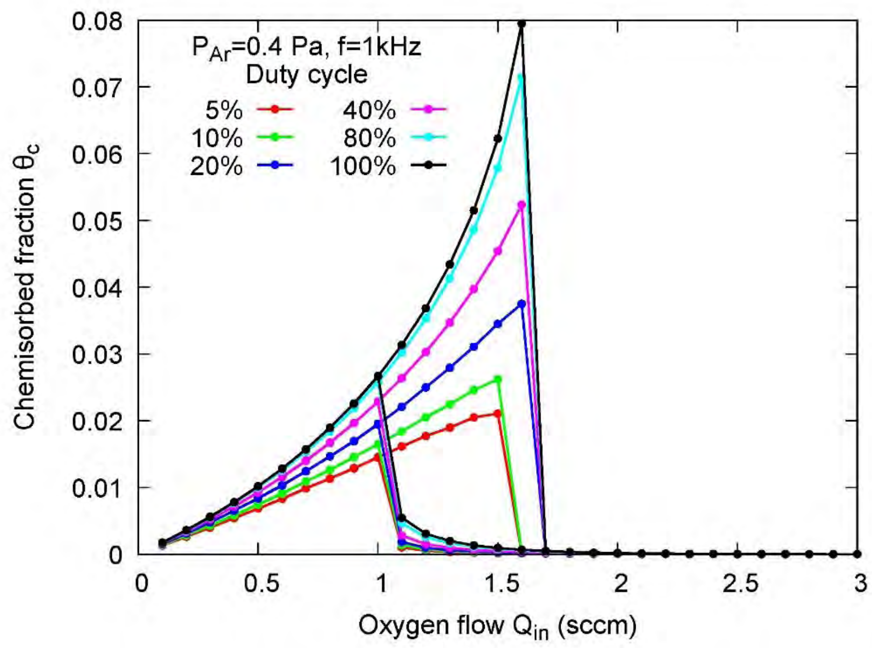
Gas reactivity

RSD^{+PR}

What's the influence of the gas reactivity?

- Sticking coefficient target & substrate: 0.1 during pulse-on time
  0.01 during pulse-off time
- Chemisorption is suppressed compared to subsurface oxidation
- Gas rarefaction would give similar behavior





Returning metal

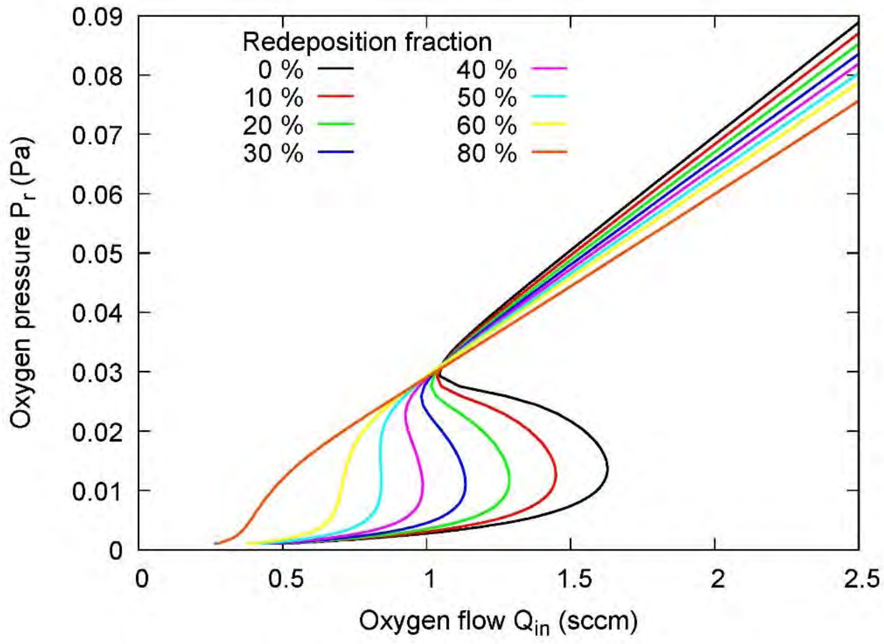
RSD

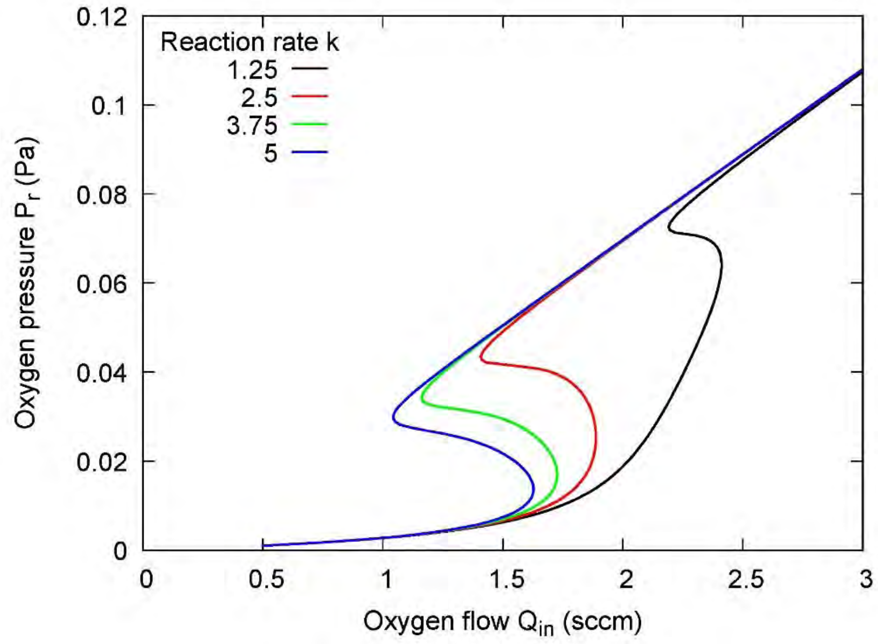
What's the influence of returning metal in DC?

☞ redeposition on the surface of neutral metal eliminates the hysteresis as the 1st critical point shifts faster than the 2nd

but for HiPIMS it are metal ions

☞ metal enrichment in subsurface equivalent with lower oxide production or reaction rate *k*





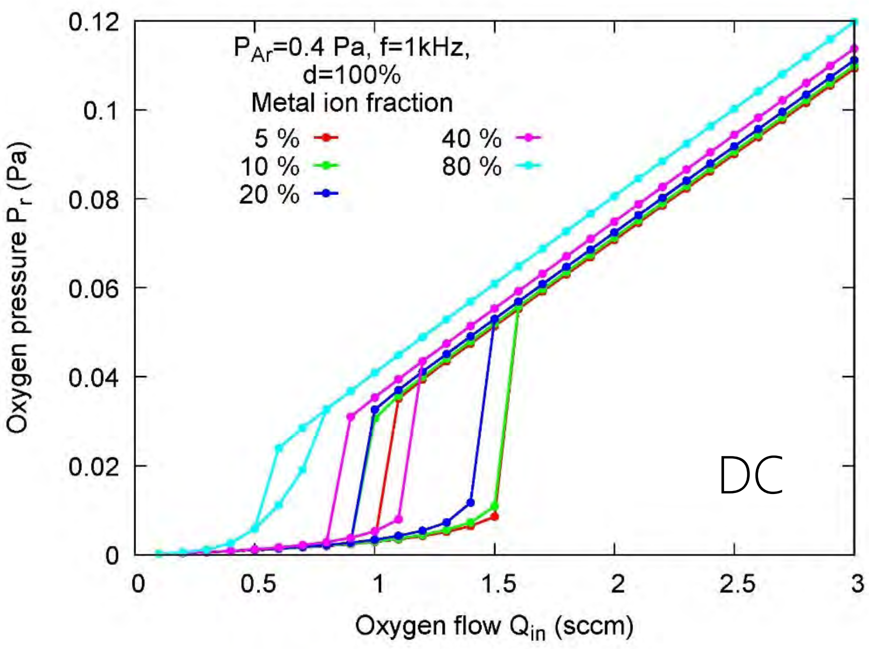
Metal implantation

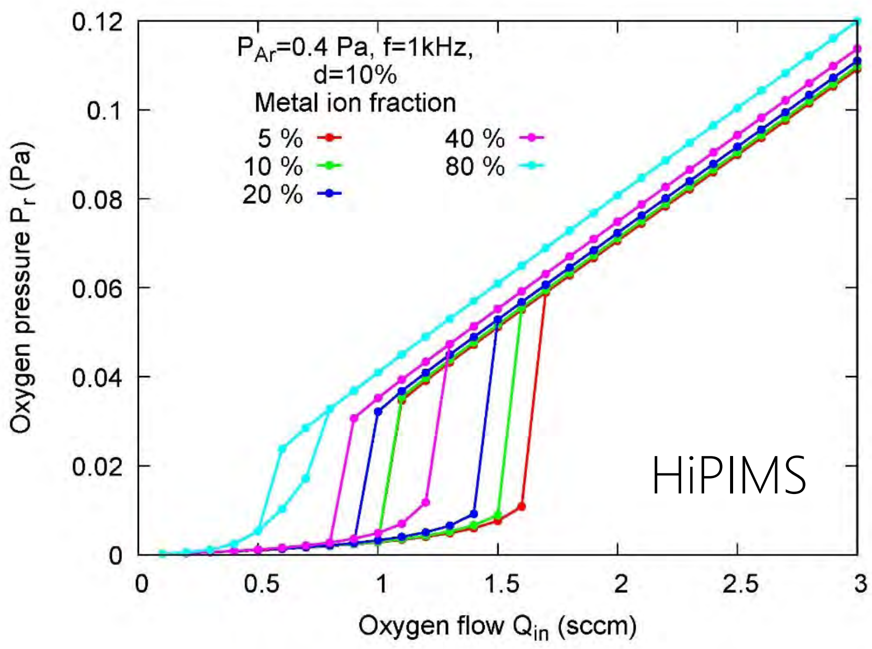
RSD^{+PM}

What's the influence of the metal implantation?

- ☞ combined effect of "redeposition" and "reaction rate"
- ☞ similar effect for DC and HiPIMS case
- ☞ hysteresis shifts to lower oxygen flows and narrows with increasing fraction of metal ions

⇨ reduction of hysteresis (but slower than only redeposition)





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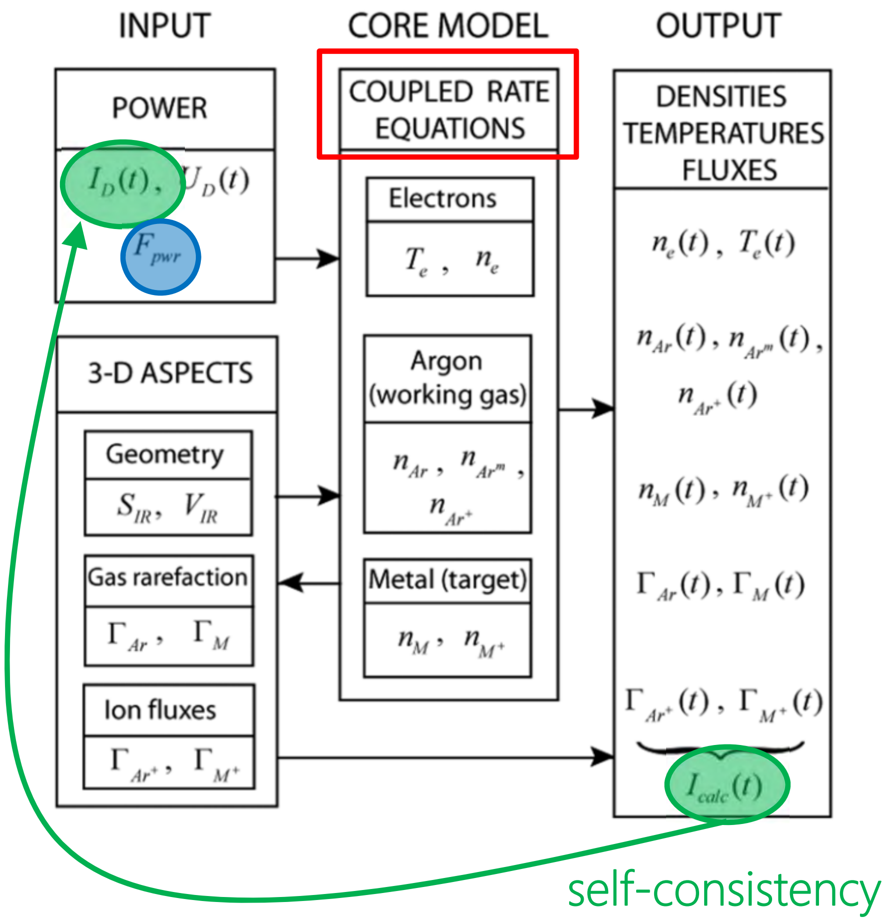
IRM for HiPIMS plasma

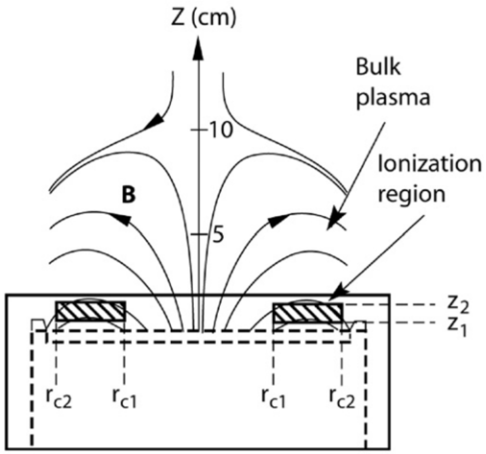


M.A. Raadu, et al., *Plasma Sources Sci. Technol.* 20 (2011) 065007

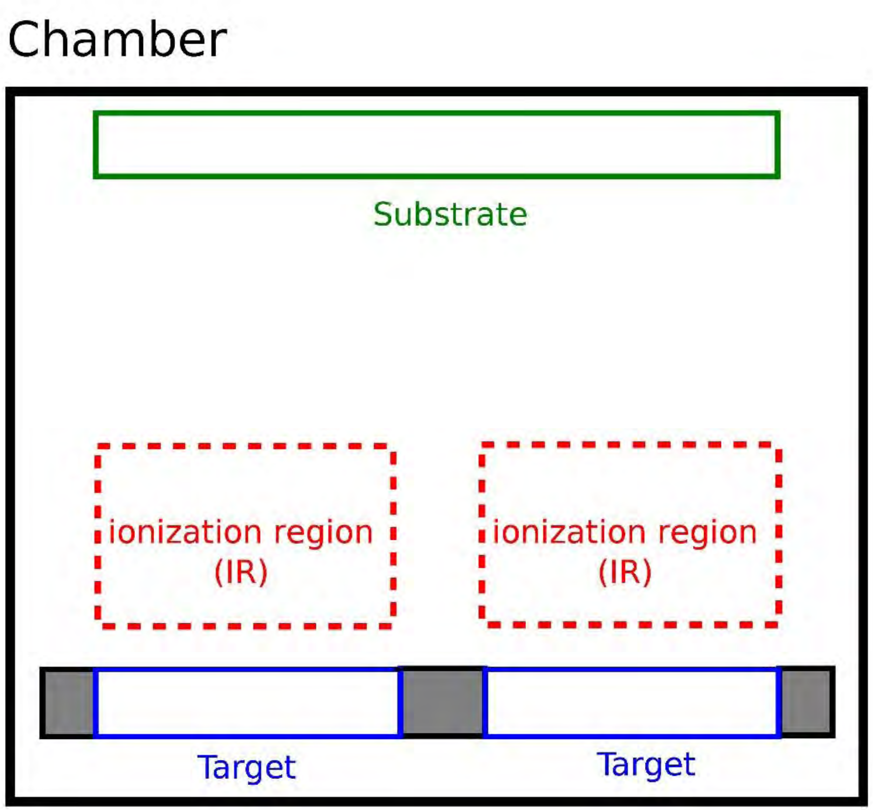
IRM
= Ionization Region Model
= global (volume-averaged) model for HiPIMS plasma

... since 2008 by Gudmundsson et al. and intensively expanded

This work "simple version" (Raadu, et al.)
ONE "true" fit parameter F_{pwr}



RSD + IRM = RSD^{+IR}

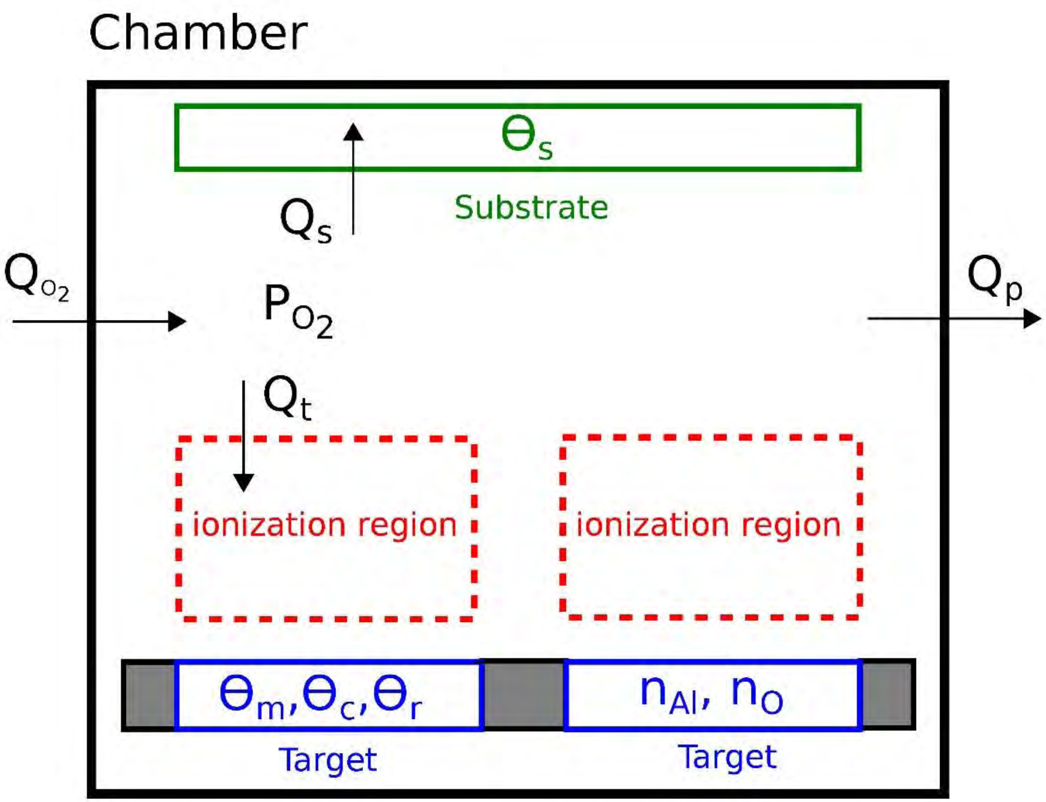


Global model
for
reactive HiPIMS deposition
=
integrate IRM into
modified RSD2013

Four system parts:

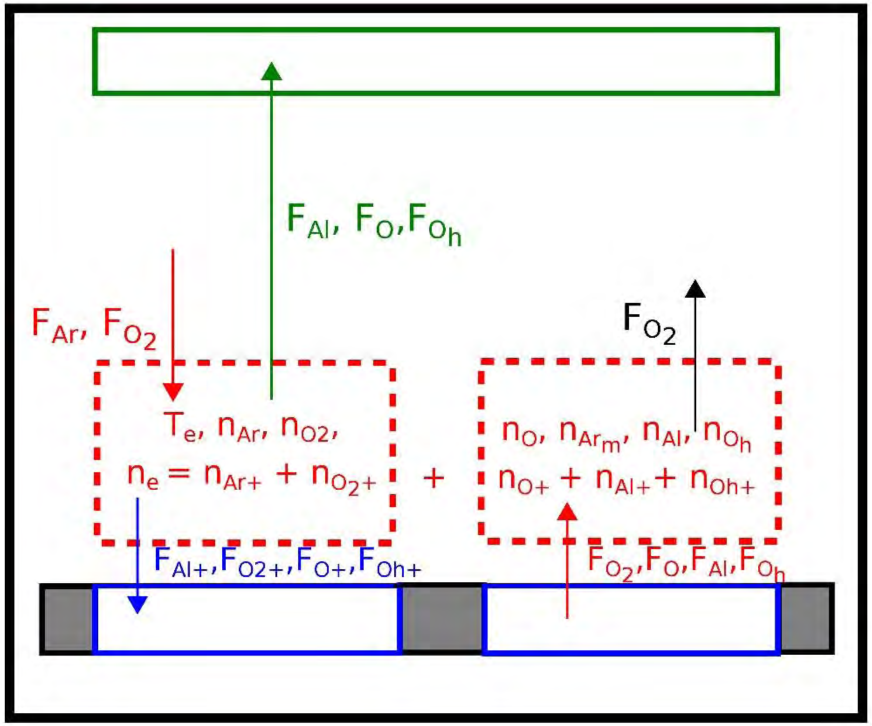
1. chamber (0 D)
2. substrate (2 D)
3. target (1D)
4. ionization region (0 D)

RSD + IRM = RSD^{+IR}



RSD variables remain
but
flow q_t into target
becomes
flow q_t into IR

RSD + IRM = RSD^{+IR}



IR species

<u>Neutrals:</u>

Ar, Ar_m, O_2, O

<u>Sputtered:</u>

Al, O_h : directed flux

<u>Ions:</u>

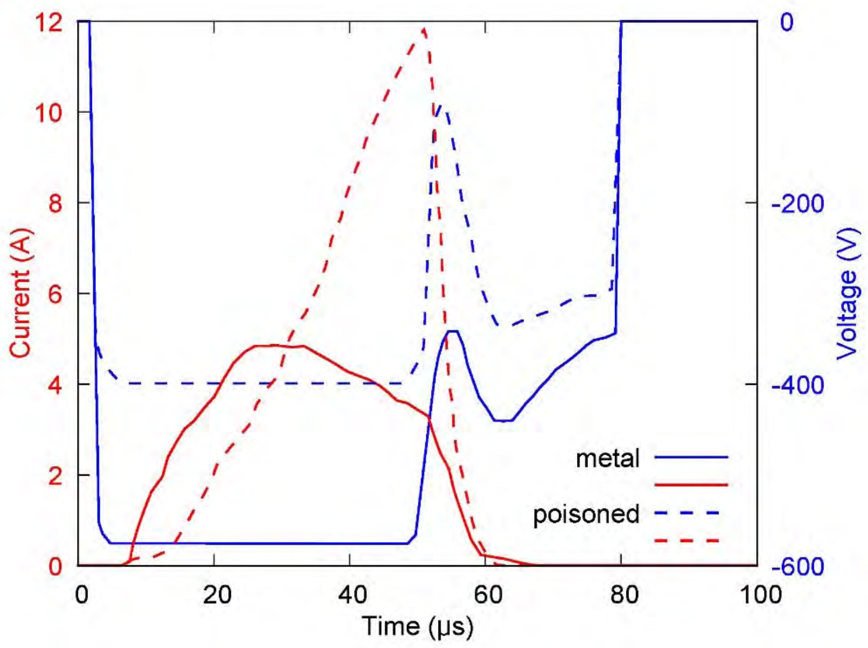
single charged

<u>Electron:</u>

T_e power balance

n_e from quasi-neutral condition

Input for RSD^{+IR}



M. Aiempanakit, et al., *J. Appl. Phys.* 113, 133302 (2013)

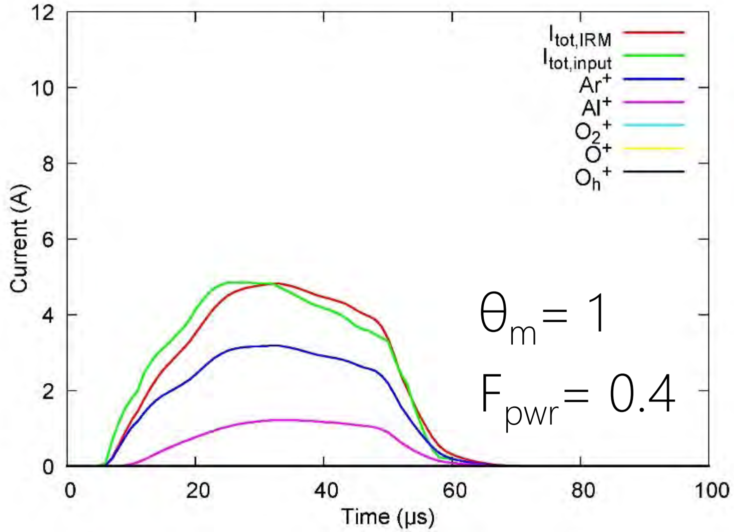
Sputter conditions:

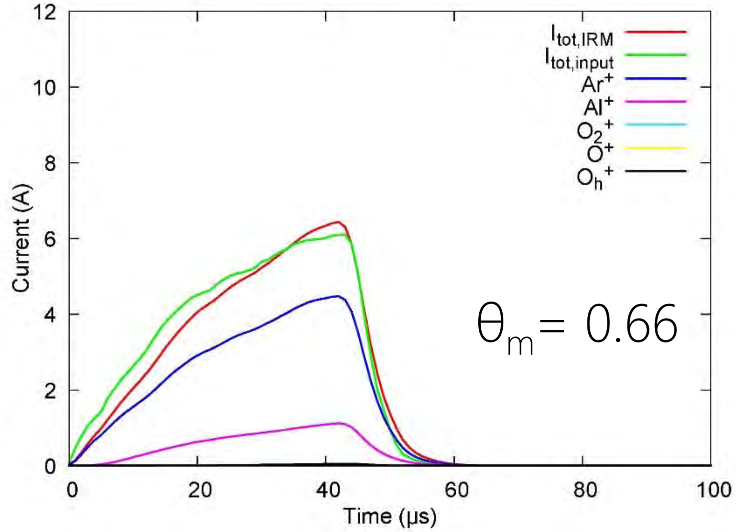
- Target Al (D = 2")
- Process gas Ar
- Reactive gas O_2
- Pumping speed S = 50 L/s
- P_{Ar} = 0.8 Pa
- Frequency 500 Hz
- Pulse width 50 μs
- Duty cycle 2,5 %

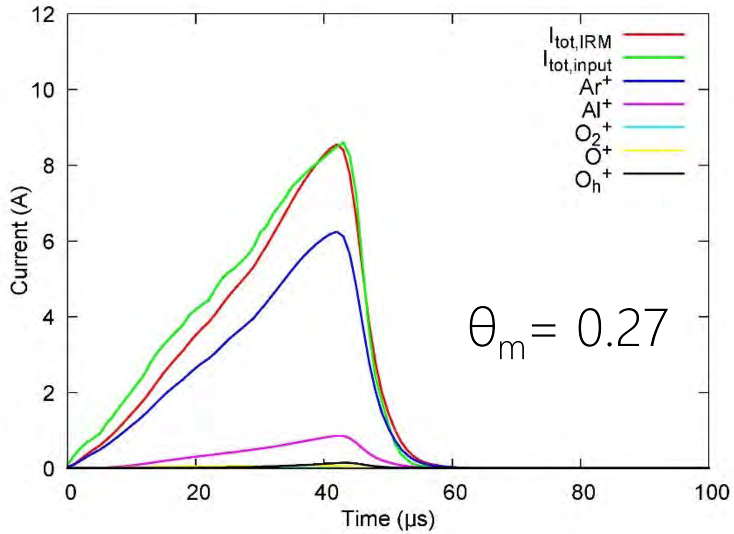
Input of IVt characteristics

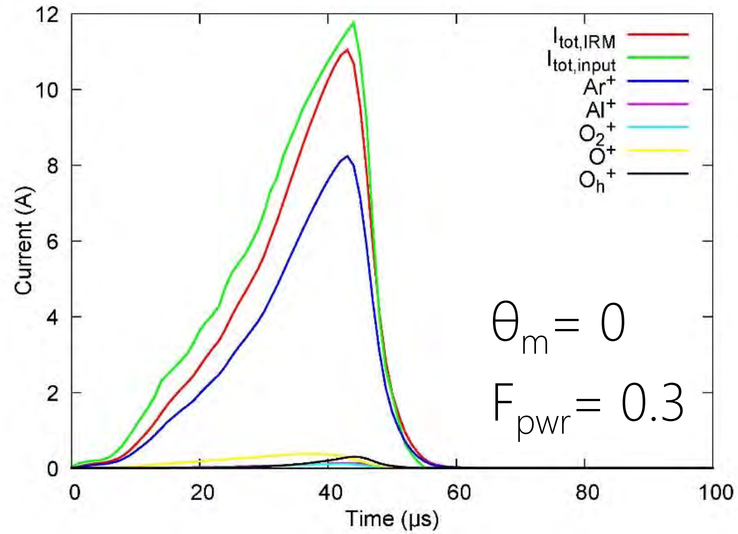
- metal (θ_m=1) and poisoned (θ_m=0) mode
- transition (0 < θ_m < 1) mode ☞ $I = I_m\theta_m + I_r(1-\theta_m)$ & $V = V_m\theta_m + V_r(1-\theta_m)$
  ☞ $F_{pwr} = F_{pwr,\,m}\theta_m + F_{pwr,\,r}(1-\theta_m)$

Locking fitting parameter F_{pwr}







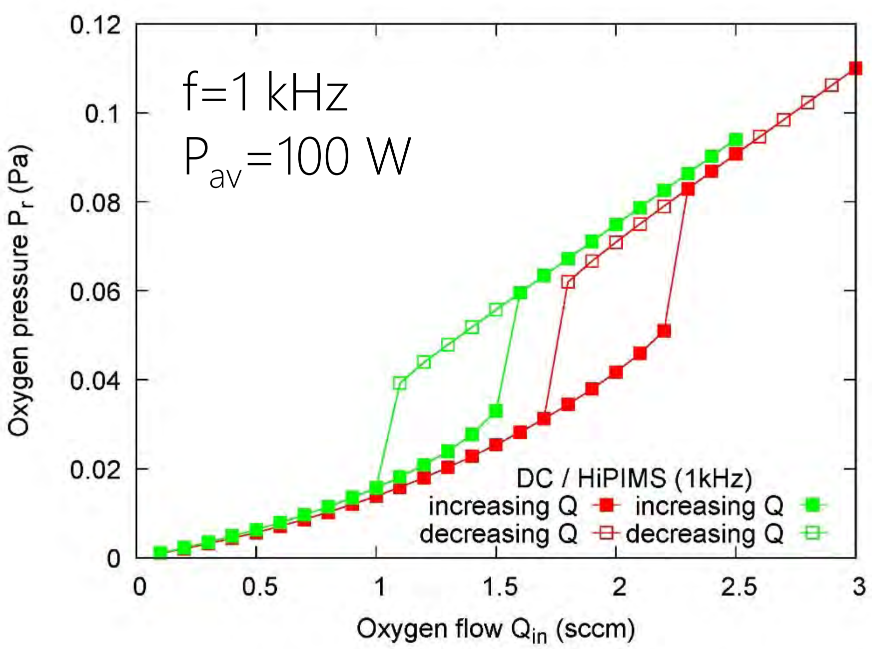


First result

RSD^{+IR}

What does this model say?

- all previous effects are now included
- hysteresis shifts to lower oxygen flows but does not narrow (yet?)
- signature of implantation of returning metal



but ...

- we chose a to simple IRM version
- ion metal fraction is only ~20 % (HiPIMS) which is expected to double
- can we transfer our model parameters from DC to HiPIMS?

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Future advances

For IR model …

- potential difference over IR
- two populations electrons "cold" and "warm"
- electron heating = sheath energization + Ohmic heating
- more species (?), more reactions (?)
- speed-up the RSD^{+IR} calculation

For a future RSD model …

- full atomic target description
- recoil/ion mixing
- (ion enhanced) diffusion processes

For experimentalists …

- a systematic survey

Conclusion

1. Knowledge of reactive DC sputtering can guide us to the unravel the **existence conditions** for a **hysteresis** during reactive HiPIMS.

2. Extensions of the RSD model are used to study the **impact of several effects** claimed to elimenate the hysteresis during reactive HiPIMS.

3. A first coupling between the **RSD2013 model** and the **IR model** is established.

4. Implantation of **ionized sputtered metal** seems to dominate the hysteresis behavior.

5. For a definite answer, **more experimental data** and **modelling** is needed.

Acknowledgements

"Target on growth"

High Performance Computing

DRAFT colleagues: